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IR plus vacuum ultraviolet spectroscopy of neutral and ionic organic acid monomers and clusters: Propanoic acid

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The vibrational spectrum of molecular propanoic acid, cooled in a supersonic expansion, in the region of 2500 to 7500 cm^{-1} is obtained employing infrared plus vacuum ultraviolet nonresonant ionization detected spectroscopy. The fundamental and first overtone of the CH and OH stretch modes of cold propanoic acid molecules can be identified in the spectrum. Propanoic acid neutral and ionic clusters are also studied employing nonresonant ion dip and photodissociation spectroscopic techniques, respectively. For the neutral dimer, a sequence of features observed at ca. 2500–2700 cm^{-1} can be assigned as combination bands of low frequency modes with the COH bending overtone; these features characterize the cyclic dimer ring structure. IR spectra of the larger neutral clusters $n=3, 4, 5$ indicate that they also have cyclic structures in which the OH groups are engaged in the cluster hydrogen bonding network. The CH groups are not involved in this hydrogen bonding structure. Free OH features are observed for the protonated ion clusters $(C_2H_5COOH)_nH^+$, $n=1,\ldots,5$, indicating that at least one OH group of these cluster ions is not involved in the cluster hydrogen bonding network. A comparison of the results for four hydrogen bonding neutral and ionic clusters (CH_3OH, C_2H_5OH, CH_3COOH, and C_2H_5COOH) is presented and discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2378628]

I. INTRODUCTION

Carboxylic acids (*R*COOH) and their clusters are of considerable interest for at least two reasons: (1) they form hydrogen bonded clusters with extended networks of hydrogen bonds generating both cyclic (neutral) and noncyclic (ionic) cluster structures[1–11] and (2) they represent model systems for many biologically interesting structures such as amino acids, peptides, and their polymers. In crystals and liquids, carboxylic acids are interlinked to form either a cyclic dimer or an infinite chain; the manner of linkage depends on the substituent *R*. Protonated carboxylic acid clusters have been studied recently by electron impact ionization and unimolecular dissociation reactions have been observed.[1,12–15] *Ab initio* calculations have also been performed: small clusters ($n \leqslant 5$) of the form $(RCOOH)_nH^+$ fragment by loss of a neutral monomer but larger clusters evaporate a neutral dimer.

One of the better methods of generating qualitative structural information on clusters in general, but hydrogen bonded clusters in particular, is through vibrational spectroscopy. Infrared (IR) spectroscopy (mid-IR, 2500–7500 cm^{-1}) of clusters can generate information on cyclic versus extended hydrogen bonded networks, which hydrogen atoms (e.g., CH or OH) are involved in the bonding, and how a proton might be shared in an ionic cluster. Mid-IR spectra of alcohols have been measured by IR plus VUV (118 nm, 10.5 eV) nonresonant ionization detected (NRID-IR) spectroscopy in our laboratory.[16,17] VUV plus IR nonresonant ion dip (NRIDip-IR) and infrared photodissociation (IRPD) spectroscopy are also quite useful for the study of neutral and cationic clusters, respectively.[18–22]

Both formic and acetic acids have been studied[23–28] previously but much less attention has been given to propanoic acid. The larger acid species are important because their behavior is more governed by the acid molecule substituent group, *R*. In this report we present the IR spectrum of propanoic monomer cooled in a supersonic expansion in the spectral region of 2500–7500 cm^{-1} detected by NRID-IR spectroscopy employ IR light and VUV light. Propanoic acid neutral and protonated cationic clusters are studied employing NRIDip-IR and IRPD spectroscopies, respectively. Cluster structure and hydrogen bonding patterns are discussed on the basis of these experimental data.

II. EXPERIMENTAL PROCEDURES

A. Generation and detection of propanoic acid molecules, clusters, and cations

The experimental apparatus used to record VUV time of flight (TOF) mass spectra and IR spectra of propanoic acid and its clusters has been described in detail previously.[29–31] Briefly, propanoic acid vapor is seeded into a Ne/He gas mixture (70%/30%, total pressure of 3 atm) and the gaseous mixture is expanded into a high vacuum chamber by a heated (50 °C) pulsed supersonic valve (Packer General Valve series 9). Thus a molecular beam containing both propanoic acid monomers and clusters is generated. The molecular beam is collimated by a conical skimmer with a 1.5 mm hole at its apex, located about 3 cm downstream from the pulsed nozzle orifice. The skimmed molecular beam is crossed per-

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[a)] Electronic mail: erb@lamar.colostate.edu pendicularly by the VUV (118 nm) laser beam in the ionization region of a time of flight mass spectrometer (TOFMS). A counterpropagating IR laser beam is focused upstream from the VUV/molecular beam intersection point by a 40 cm focal length lens to access neutral ground state species and at the intersection of the VUV and the molecular beam to access ionic species. Generation of the VUV 118 nm light and IR laser light is similar to that described earlier.[30,31] The 118 nm radiation is the ninth harmonic of the fundamental output of a Nd^{+3}/yttrium aluminum garnet (YAG) laser at 1.064 μm. 355 nm radiation (third harmonic) is focused into a cell with Xe/Ar ratio of 1:10 at ca. 200 Torr total pressure. A MgF_2 lens focuses the 118 nm light in the ionization region of the TOFMS and disperses the remaining 355 nm light. Tunable IR light output in the range of the mid-IR and near IR has a pulse energy of 3–5 mJ/pulse and a bandwidth of $\sim 2\ cm^{-1}$.

B. IR+VUV IR spectroscopy detection of propanoic acid molecules, clusters, and cations

The VUV single photon (118.2 nm, 10.487 eV) is on the threshold of the ionization energy (IE) of propanoic acid.[32] While the IR laser is scanned to excite expansion cooled propanoic acid molecules to vibrationally excited levels, the total energy in the molecule, $h\nu_{IR}+h\nu_{VUV}$, is higher than the IE, and hence vibrationally excited molecules can be ionized by absorption of a 10.487 eV VUV photon. With this approach, OH and CH stretch and overtone modes of propanoic acid molecules are recorded as an increase of the monomer ion mass channel signal.

IR spectroscopy of neutral and ionic clusters of propanoic acid is developed based on vibrational predissociation spectroscopy of weakly bound clusters.[33–36] Previous studies[16,17] show that neutral acid, alcohol, and other van der Waals clusters formed in a supersonic expansion can be ionized by a VUV (118 nm) single photon and that the ionized neutral cluster undergoes a rapid (<1 ns) proton transfer reaction and fragmentation of the following nature:

$$(R\mathrm{OH})_n \underset{118\ \mathrm{nm}}{\overset{h\nu}{\rightarrow}} (R\mathrm{OH})_n^+ + e^- \rightarrow (R\mathrm{OH})_{n-1}\mathrm{H}^+ + e^- + R\mathrm{O}. \tag{1}$$

The IE of propanoic acid [10.5 eV (Ref. 29)] is close to that of alcohols, and thus similar results can be anticipated for propanoic clusters. Previous studies[31,37] show that the protonated cluster ions, generated through proton transfer reactions following VUV single photon ionization, essentially correlate to the neutral clusters as indicated above. The time scale for this fragmentation reaction, driven by the heat of the proton transfer reaction, is approximately in the picosecond range. Fragmentation between ca. 1 ns and 2 μs would occur in the ion extraction region of the TOFMS and would cause an asymmetric linewidth for the mass features that is not observed. Calculations of the thermodynamics for water and alcohol clusters[37] further support this result.

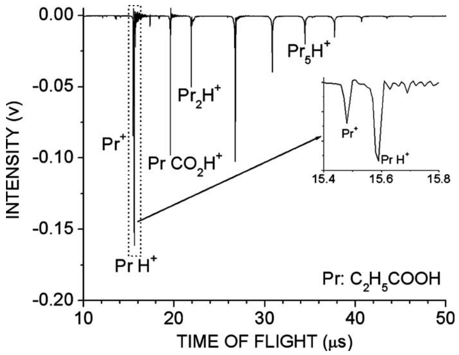


FIG. 1. TOF mass spectrum of propanoic acid clusters generated by VUV (118 nm) single photon ionization.

If the tunable IR light pulse is introduced into the molecular beam ca. 50 ns prior to the VUV pulse, IR absorption will induce photodissociation of the neutral propanoic acid clusters leading to a reduction of $(C_2H_5COOH)_n$ concentration in the beam and a reduction of the $(C_2H_5COOH)_{n-1}H^+$ ion channel signal. Thus by scanning the IR wavelength while monitoring the $(C_2H_5COOH)_{n-1}H^+$ ion signal intensity, a mass selective NRIDip-IR spectrum for the neutral cluster $(C_2H_5COOH)_n$ is obtained as an IR ion signal "dip" spectrum. Similarly, if tunable IR light is introduced with a delay time with respect to the VUV laser pulse of ca. 30 ns, mass selected IRPD spectra of cluster ions are obtained as an ion dip spectrum for the $(C_2H_5COOH)_nH^+$ mass channel.

III. RESULTS AND DISCUSSION

A. VUV (118 nm) single photon ionization of propanoic acid clusters

Figure 1 presents the time of flight mass spectrum of the propanoic acid hydrogen bonded clusters through 118 nm single photon ionization. The main cluster series observed is $(C_2H_5COOH)_nH^+$. Note that the VUV photon energy is just at the threshold of the propanoic molecule IE and the weak molecular parent cation can be observed as a minor signal on the side of the neutral dimer $(C_2H_5COOH)H^+$ signal. Clusters $(C_2H_5COOH)_n$ have lower IEs than the monomer, and can easily be ionized at 10.5 eV single photon energy. Protonated clusters $(C_2H_5COOH)_nH^+$ are generated from the neutral cluster $n+1$ through proton transfer and fragmentation $[(C_2H_5COOH)_{n+1}+h\nu(118\ \mathrm{nm})\rightarrow(C_2H_5COOH)_nH^+ +C_2H_5COO+e^-]$ following ionization.

The mass spectrum of Fig. 1 shows another intense feature identified as $(C_2H_5COOH)COOH^+$. The intensity ratio of this feature to the other features arising from the neutral dimer $(C_2H_5COOH)H^+$ is 2:3. Similar results are observed for acetic acid and ethanol clusters. These features arise generally from a β-CC bond fission reaction in the ionized neutral dimer. Two pathways can be identified for the ion molecule reaction of the dimer under VUV single photon ionization. One pathway generates (C_2H_5COOH) $COOH^+$ cations and C_2H_5 radicals. This pathway has the lower heat of reaction as determined by density functional theory calculations (see Table I). The second pathway for this fragmentation reaction is the generation of the protonated cluster ion and the C_2H_5COO radical. Both reaction energies are presented in Table I based on a B3LYP/aug-cc-pVDZ density

TABLE I. Heat of reaction for the ionization and ion molecule reactions of the proipanoic acid dimer obtained from a DFT calculation at the B3LYP/aug-pVDZ level. [The default self-consistent field (SCF) method is converged to either 10^{-4} fot both the energy and density or 10^{-5} on the energy whichever happens first. The "fine" integration grid is the default for this calculation.]

Reaction	ΔH (eV)
$(C_2H_5COOH)_2 \rightarrow (C_2H_5COOH)_2^+ + e^-$	9.35
$(C_2H_5COOH)_2 \rightarrow (C_2H_5COOH)COOH^+ + C2H5 + e^-$	9.41
$(C_2H_5COOH)_2 \rightarrow (C_2H_5COOH)H^+ + C_2C_5COO + e^-$	10.42

functional theory (DFT) calculation for the dimer ion reaction. For larger clusters than the dimer only the proton transfer channel appears to be open. This implies that the proton affinities (PAs) of clusters $(C_2H_5COOH)_n$, $n > 1$, are larger than that of the monomer, and that this pathway is much more favorable and has a lower reaction barrier for larger clusters. The calculation gives the reaction thermodynamics qualitatively but not the reaction surfaces or barriers, and thus does not necessarily predict the relative mass spectral peak intensities.

B. IR+VUV (118 nm) NRID-IR spectroscopy of propanoic acid molecules

As mentioned above, VUV 118 nm single photon is on the threshold of the IE of the propanoic acid monomer with mid-IR photons (0.35–0.7 eV) added to the molecule; the total energy in the molecule is in excess of the IE and can hence increase the ionization efficiency for the molecule. The mass spectrum shown in Fig. 2(a) displays this result: the ion current for propanoic acid cations (Pr^+, $C_2H_5COOH^+$) is significantly increased in the mass spectrum if resonant IR light is introduced into the experiment. Figure 2(b) presents the IR+VUV NRID-IR spectroscopy of the propanoic acid monomer. Features located at ca. 3581 and 6991 cm^{-1} can be assigned as OH stretch fundamental (ν_{OH}) and first overtone ($2\nu_{OH}$), respectively.[38] Reference 38 presents the complete spectral range of 2500–7000 cm^{-1} for propanoic acid. Four resolved features are observed located at ca. 3000 cm^{-1} (2890, 2932, 2952, 2988 cm^{-1}); these are identified as CH fundamental stretches (ν_{CH}). The weak features at ca. 5800 cm^{-1} are due to the ν_{CH} first overtone ($2\nu_{CH}$).

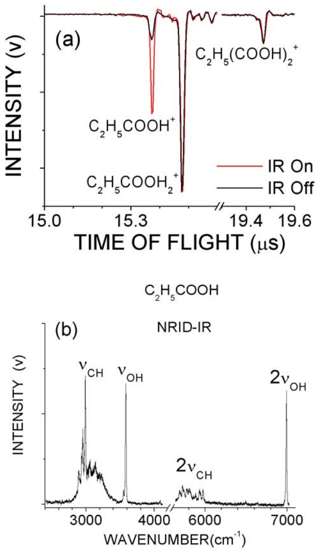


FIG. 2. Mid-IR (2700–7100 cm^{-1}) vibrational spectrum of propanoic acid monomer detected by NRID-IR spectroscopy using propanoic acid vapor seeded in 3 atm of a He/Ne mixture and expanded into the vacuum (b). The omitted range in the IR spectrum contains weak combination and overtone features. (a) contains the mass spectrum of $C_2H_5COOH^+$ and $C_2H_5COOH_2^+$ with the presence (red line) and absence (black line) of IR light.

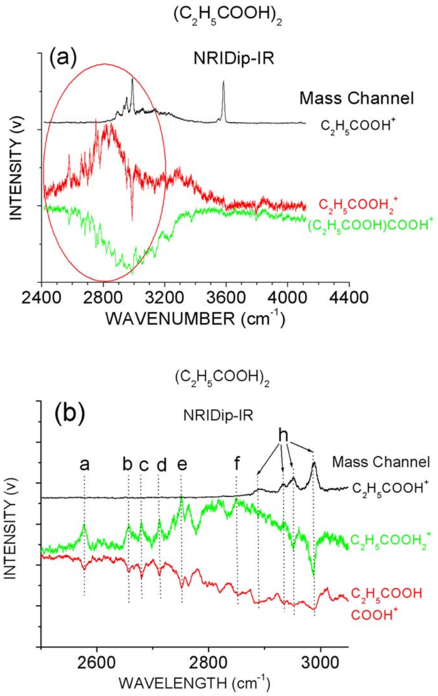


FIG. 3. Vibrational spectra of the neutral monomer and dimer of propanoic acid employing NRIDip-IR spectroscopy and monitoring the mass channels CH_3COOH^+, $CH_3COOH_2^+$, and $CH_3COOH-COOH^+$ in the regions of (a) 2400–4200 cm^{-1} and (b) 2500–3100 cm^{-1}. Band a, 2 δCOH; b, 2 $\delta_{COH}+\beta$; c, 2 $\delta_{COH}+\gamma$; d, 2 $\delta_{COH}+2\beta$; e, 2 $\delta_{COH}+\nu_{OO}$; f, ν_{OH}; bonded OH stretch; h, ν_{CH}, free CH stretch; δ COH:COH bending; β, in-plane ring deformation; γ, out-of-plane ring deformation; ν_{OO}, OO stretch. Assignments are based on a comparison with the similar region for acetic acid. See Ref. 30 for comparison.

C. VUV+IR NRIDip-IR spectroscopy of the propanoic acid neutral clusters

Mass selective photodissociation spectroscopy has been applied to the study of the propanoic acid dimer generated in the supersonic expansion. Figure 3(a) presents IR spectra (NRIDip-IR) of the neutral dimer by monitoring the mass channels $(C_2H_5COOH)H^+$ and $(C_2H_5COOH)COOH^+$. The two neutral dimer spectra displayed in Fig. 3 and monitored in the different mass channels are nearly identical except for the sign. The spectrum obtained by monitoring mass channel PrH^+ is shown as an "enhancement" while that obtained monitoring mass channel $PrCOOH^+$ is shown as a dip. The two sharp features in Fig. 3(a) detected in the PrH^+ mass channel (2988 and 2952 cm^{-1}) can be assigned as the CH stretches of the dimer, since they are nearly identical to CH transitions of the monomer. The sign of these signals sug-

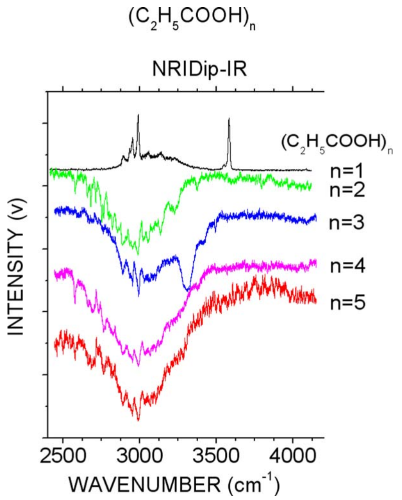


FIG. 4. The CH and OH stretch fundamental vibrations of neutral propanoic acid clusters, $(C_2H_5COOH)_n$, for $n=1$ (top) to 5 (bottom), recorded by NRIDip-IR spectroscopy through monitoring $C_2H_5COOH^+$, $(C_2H_5COOH)COOH^+$, and $(C_2H_5COOH)_{n-1}H^+$ signals generated by VUV laser ionization.

gests that with IR energy absorbed ca. 3000 cm^{-1}, the PrH^+ cluster ion can fragment to another mass channel and that with the same energy the $PrCOOH^+$ cluster ion fragments to the PrH^+ mass channel. Note that these particular CH stretch features are quite intense in the Pr^+ and PrH^+ mass channels. These results suggest that the CH structures of Pr are not perturbed very much in the dimer and thus the CH moieties are not involved in the (hydrogen) bonding structure of the cluster. In the range of 2500–2800 cm^{-1}, some characteristic features are assigned as combination bands of the low frequency (intracluster) modes of the cyclic dimer ring with the COH bending overtone [see Fig. 3(b)]. Similar results are obtained for the acetic acid dimer.[29] Possible detailed assignments are given in Fig. 3(b): δ_{COH} represents the COH bend, β represents the in-plane dimer ring deformation, γ represents the out-of-plane ring deformation, and ν_{OO} represents the OO stretch motion. The bonded OH stretch can be observed at ca. 2850 cm^{-1}.

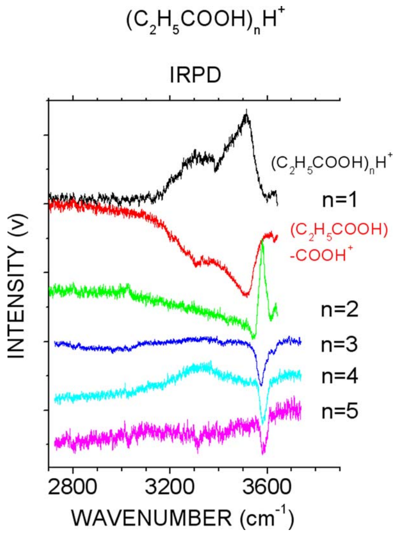
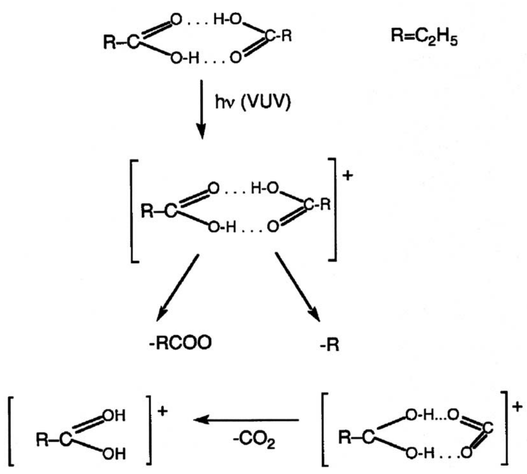


FIG. 5. The CH and OH stretch fundamental vibrations of propanoic cluster cations $(C_2H_5COOH)COOH^+$ and $(C_2H_5COOH)_nH^+$ [$n=1$ (top) to 5 (bottom)], recorded by IRPD spectroscopy. Parent cation signals generated by VUV laser ionization are monitored in the indicated mass channels.



SCHEME 1.

Figure 4 presents the NRIDip-IR spectrum of neutral propanoic acid clusters $(C_2H_5COOH)_n$, $n=1-5$, obtained by monitoring the $(C_2H_5COOH)_{n-1}H^+$ mass channel, for $n \geqslant 2$: monomer spectra are detected in the $C_2H_5COOH^+$ and dimer spectra are monitored in the $(C_2H_5COOH)COOH^+$ mass channels, respectively. Similar to the spectra of alcohol clusters,[16,17] the absence of free OH features in the IR spectra of the clusters reveals that all the OH groups are involved in cluster bonding. The one resolved intense dip feature at 3312 cm^{-1} for the trimer is assigned the cluster bonded OH motion. OH bonded modes in larger clusters are more redshifted and converge to ca. 3000 cm^{-1} for $n=5$. These latter features eventually overlap with the CH modes in this region. The CH modes apparently do not shift for these clusters.

D. VUV+IR spectroscopy of propanoic acid cluster cations

Mass selective IRPD spectra of $PrCOOH^+$ and the sequence of protonated propanoic acid clusters PrH^+, $n=1,\ldots,5$, for the CH and OH fundamental stretch region are presented in Fig. 5. These spectra are obtained monitoring the parent ion mass channels indicated above. The IRPD spectra for the mass channels PrH^+ and $PrCOOH^+$ are very similar and this can occur by two mechanisms: the ion $PrCOOH^+$ fragments into the PrH^+ mass channel due to IR absorption and/or the two separate species have similar spectra. Note that without IR radiation present [see Figs. 1 and 2(a)] the PrH^+ signal is still quite intense. Scheme 1 gives a

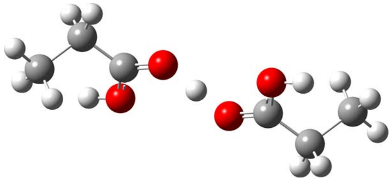


FIG. 6. Schematic drawing of the propanoic acid protonated dimer ion.

TABLE II. Vibrational energies of the OH and CH stretches of the alcohols and organic acids (cm^{-1}). (See Refs. 16, 17, and 29.)

	OH stretch		CH stretch		
	Fundamental	Overtone	Fundamental	Overtone	Combination
CH_3OH	3684	7196	2952	5820	3922, CH fundamental and OH torsion
C_2H_5OH	3667, 3682	7174, 7179	2900, 3000	5795	3886; 6140; 6321; 6571; unassigned
CH_3COOH	3585	6999	3015	6000	4134, OH stretch and OH torsion; 5378, OH stretch and CO stretch.
C_2H_5COOH	3581	6991	2940	5800	

graphical representation of these ideas. In the first instance the spectra of $PrCOOH^+$ overwhelms (note the sign change) the PrH^+ spectrum and in the second instance, the $PrCOOH^+$ spectrum is still dominant (again, sign) but both species contribute to the overall band shape. The conclusion is, of course, the latter. The features at 3514 cm^{-1} can be assigned as the free OH stretch and the broad peaks at ca. 3263 cm^{-1} arise from the bonded OH stretch.

The spectrum of the protonated dimer Pr_2H^+ ($n=2$ in Fig. 5) has a free OH stretch contribution as a dip feature near 3575 cm^{-1} that has been distorted (or nearly overwhelmed) by a positive peak at ca. 3580 cm^{-1}. This latter spectral contribution comes from the dissociation of larger cluster ions (e.g., $n=3,4,5$, see Fig. 5). This observation suggests that the protonated dimer has a relatively stable and symmetric structure: the two molecules in the protonated dimer share the proton equally (see Fig. 6). For large protonated clusters Pr_nH^+, $n=3,\ldots,5$, the relatively sharp features at ca. 3574($n=3$), 3586($n=4$), and 3586($n=5$) cm^{-1} can be assigned as free OH stretch vibrations of their respective cluster cations.

IV. COMPARISONS OF HYDROGEN BONDED NEUTRAL AND IONIC CLUSTERS

Spectroscopic information about gas phase hydrogen bonded clusters is of considerable interest for the study of intermolecular interactions, development of intramolecular structure, chemical reactions, and photochemistry. We have reported sequences of observations on alcohols and carboxylic acids by VUV single photon ionization and VUV+IR spectroscopy. We summarize and compare and contrast these results in the ensuing discussion. VUV single photon ionization represents a "soft" ionization source for small organic molecules and clusters with minimal fragmentation[29–31] because the single photon energy is less than a few eV within the vertical ionization energy (VIE) threshold for the species of interest. Studies demonstrate[37,39,40] that protonated clusters ($R_{n-1}H^+$, $R=R'OH$, $R'COOH$) originate from the neutral R_n clusters. Another common phenomenon for this cluster series is characterized for the dimer ion reaction pathway involving β-CC bond fission. This suggests that the VUV excitation for the dimer is below or near the proton transfer barrier for the ion R_2^+: VUV excitation, R PA, and the VIE/adiabatic IE difference select for this alternate ion molecule reaction following ionization.[37]

Table II contains a comparative listing of the OH, CH, and overtone features of the four systems CH_3OH, C_2H_5OH, CH_3COOH, and C_2H_5COOH. The results show a redshift for the OH mode energies as a function of side chain length for both the carboxylic acids and the alcohols. This redshift implies that an increase in hydrocarbon chain length for the alcohols and carboxylic acids generates a significant decrease in OH bond strength.

Carboxylic acid molecules in the neutral dimer form a symmetric, cyclic structure via double hydrogen bonds with characteristic features of ca. 2500–2900 cm^{-1}. On the other hand, alcohol dimers display both free and bonded OH modes and thus those dimers have one bonded and one free OH group with a chainlike structure. Summaries of those data are presented in Table III for alcohols and Table IV for carboxylic acids.

These four monomers reveal similar behavior for larger neutral clusters ($n>2$) as well. Both alcohol and carboxylic acid neutral clusters larger than the dimer display bonded OH mode spectra only. These features redshift with cluster size and converge to ca. 3300 cm^{-1} for the alcohols and to 3000 cm^{-1} for the acids. The CH stretch modes of those clusters, however, do not shift with cluster size. The evidence suggests that a closed cyclic structure exists for all these larger clusters ($n>2$) and that only the OH group is involved in the hydrogen bonded cluster network. These structures are different from those found in the comparable liquids and crystals.[1,12] The increasing redshift with increasing cluster size and with side chain length indicates a strengthening of the hydrogen bonding for these clusters. Note that the bandwidth of these features is also increasing with n and side chain length and this can suggest the presence of more isomers for the larger species.

Structures of the protonated alcohol and carboxylic acid

TABLE III. Vibrational energies of the free and bonded OH stretches of the alcohol dimers (cm^{-1}). (See Refs. 16, 17, and 30.)

Modes	Bonded OH	Free OH
$(CH_3OH)_2$	3576	3679
$(C_2H_5OH)_2$	3573	3678

TABLE IV. Frequencies of the characteristic combination bands of the organic acid dimers (cm^{-1}). See text and Fig. 3 caption for definitions of symbols.

Modes	$2\delta_{\text{COH}}$	$2\delta_{\text{COH}}+\beta$	$2\delta_{\text{COH}}+\gamma$	$2\delta_{\text{COH}}+2\beta$	$2\delta_{\text{COH}}+\nu_\infty$	Bonded ν_{OH}
$(CH_3COOH)_2$	2594	2661	2721	2742	2762	2930
$(C_2H_5COOH)_2$	2578	2658	2680	2712	2751	2850

clusters, on the contrary, appear to be much different than those of the comparable neutral clusters as reflected in the general IR spectra. The free OH mode of the RH^+ clusters, identified in their IR spectra, indicates that at least one of the OH moieties is not involved in the hydrogen bonding network of small ($n=2,\ldots,5$) cluster ions. The blueshift of the free and bonded OH stretches with increasing cluster size suggests a weakening of the hydrogen bonding interactions for larger clusters. The free OH mode transition disappears at $n\geqslant 6$ for protonated acetic acid clusters and a closed cyclic structure for those larger cluster ions is identified. Recall that the free OH band for methanol cluster ions can be observed at $n=7$. Although some reports have suggested a bicyclic structure for the protonated methanol cluster ion $(CH_3OH)_7H^+$, our results show that at least one OH group for this cluster ion is not bound in hydrogen bonding. CH groups do not vary with cluster size n for any of the protonated cluster ions and one can conclude that the CH groups are not involved in the cluster hydrogen bonding network of the protonated cluster. This can also be concluded for neutral clusters.

IR spectra of the protonated dimer show that the free OH dip bands are distorted by a sharp positive feature coincident with larger cluster ion absorption. The larger protonated cluster ions (R_nH^+, $n>2$) will lose $n-2$ monomers (R) induced by (multiphoton) IR absorption. This fragmentation and spectral overlap implies that the protonated dimer is an especially stable structure ($R\text{–}H^+\text{–}R$, $R=R'OH$, $R'COOH$), in which the excess proton is equally shared between two monomers (see Fig. 6). This "Zindel-type" ion core structure has been suggested as a fundamental building block in many hydrogen bonding networks, especially that of water.[41–43]

V. CONCLUSIONS

Mass spectra of propanoic acid hydrogen bonded clusters created in a supersonic expansion are recorded by TOFMS employing ionization by 118 nm radiation. Besides the one primary, protonated cluster ion sequence $(C_2H_5COOH)_nH^+$ observed, one intense peak corresponding to $(C_2H_5COOH)COOH^+$ is evident in the spectrum. This latter feature arises from cleavage of the β-CC bond in the propanoic acid dimer ion, $(C_2H_5COOH)_2^+$. Absence of fragment cluster ions of the form $(C_2H_5COOH)_{n-1}COOH^+$ from larger clusters $(C_2H_5COOH)_n$ ($n>2$) suggests that proton affinities of clusters $(C_2H_5COOH)_n$ ($n\geqslant 2$) are larger than that of the monomer.

Analysis of IR spectra of these neutral clusters in both the CH and OH vibrational regions suggests that the dimer has a cyclic ring structure. IR spectra of larger neutral clusters ($3<n\leqslant 5$) indicate that these clusters also have a cyclic ring structure with all OH groups involved in the hydrogen bonding cluster network. The CH moieties of these neutral clusters are apparently not involved in this hydrogen bonding interaction. The free OH features observed in the IR spectra of protonated cluster ions $(C_2H_5COOH)_nH^+$ ($n=1,\ldots,5$) indicate that at least one OH group is not bonded in these cluster ions. The CH groups of these ions are also free from the hydrogen bonded network.

Comparison of the mass selected IR spectra of four typical hydrogen bonded clusters (methanol, ethanol, acetic acid, and propanoic acid) demonstrates that neutral clusters have closed cyclic structures that are bonded mostly by $OH\cdots O$ hydrogen bonds. On the other hand, IR spectra of small protonated cluster ions ($n<6$) demonstrate that at least one OH group in the ionic cluster is not involved in the hydrogen bonding network.

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[1] L. Leiserowitz, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **32**, 775 (1976).
[2] K. D. Cook and J. W. Taylor, Int. J. Mass Spectrom. Ion Phys. **35**, 259 (1980).
[3] Y. Mori and T. Kitagawa, Int. J. Mass Spectrom. Ion Process. **64**, 169 (1985).
[4] Y. Mori and T. Kitagawa, Int. J. Mass Spectrom. Ion Process. **84**, 305 (1988).
[5] Y. Mori and T. Kitagawa, Int. J. Mass Spectrom. Ion Process. **84**, 330 (1988).
[6] R. Sievert, I. Cadez, J. Van Doren, and A. W. Castleman, Jr., J. Phys. Chem. **88**, 4502 (1984).
[7] R. G. Keesee, R. Sievert, and A. W. Castleman, Jr., Ber. Bunsenges. Phys. Chem. **88**, 273 (1984).
[8] M. Meot-Ner, J. Am. Chem. Soc. **114**, 3312 (1992).
[9] M. Tsuchiya, S. Teshima, A. Shigihara, and T. Hirano, J. Mass Spectrom. Soc. Jpn. **46**, 483 (1998).
[10] N. Nishi, T. Nakabayashi, and K. Kosugi, J. Phys. Chem. A **103**, 10851 (1999).
[11] J. Karle and L. O. Brockway, J. Am. Chem. Soc. **66**, 574 (1944).
[12] T. Nakabayashi, K. Kosugi, and N. Nishi, J. Phys. Chem. A **103**, 8595 (1999).
[13] W. Y. Feng and C. Lifshitz, J. Phys. Chem. **98**, 6075 (1994).
[14] C. Lifshitz and W. Y. Feng, Int. J. Mass Spectrom. Ion Process. **146/147**, 223 (1995).
[15] R. Zhang and C. Lifshitz, J. Phys. Chem. **100**, 960 (1996).
[16] Y. J. Hu, H. B. Fu, and E. R. Bernstein, J. Chem. Phys. **125**, 154306 (2006).
[17] Y. J. Hu, H. B. Fu, and E. R. Bernstein, J. Chem. Phys. **125**, 154305 (2006).
[18] L. I. Yeh, M. Okumura, J. D. Myers, J. M. Price, and Y. T. Lee, Chem. Phys. **91**, 7319 (1989).
[19] E. J. Bieske and J. Maier, Chem. Rev. (Washington, D.C.) **93**, 2603 (1993).
[20] J. M. Lisy, *Cluser Ions* (Wiley, Chichester, UK, 1993), p. 217.
[21] K. Ohashi, H. Izutsu, Y. Inokuchi, K. Hino, N. Nishi, and H. Sekiya,

Chem. Phys. Lett. **321**, 406 (2000).
[22] K. Ohashi, Y. Inokuchi, H. Izutsu, K. Hino, N. Yamamoto, N. Nishi, and H. Sekiya, Chem. Phys. Lett. **323**, 43 (2000).
[23] J. S. Francisco, J. Chem. Phys. **96**, 1167 (1992).
[24] M. Freytes, D. Hurtmans, S. Kassi, J. Lievin, J. V. Auwera, A. Campargue, and M. Herman, Chem. Phys. **283**, 47 (2002).
[25] J. E. Headrick, Ph.D. thesis, University of Colorado, 2002.
[26] K. R. Lange, N. P. Wells, K. S. Plegge, and J. A. Phillips, J. Phys. Chem. A **105**, 3481 (2001).
[27] Y. Marechal, J. Chem. Phys. **87**, 6344 (1987).
[28] T. L. Tan, K. L. Goh, P. P. Ong, and H. H. Teo, J. Mol. Spectrosc. **202**, 194 (2000).
[29] Y. J. Hu, H. B. Fu, and E. R. Bernstein, J. Chem. Phys. **125**, 184308 (2006), preceding paper.
[30] Y. Matsuda and E. R. Bernstein, J. Phys. Chem. A **109**, 3803 (2005); D. N. Shin, Y. Matsuda, and E. R. Bernstein, J. Chem. Phys. **120**, 4157 (2004).
[31] Y. J. Hu, H. B. Fu, and E. R. Bernstein, J. Phys. Chem. A **110**, 2629 (2006); H. B. Fu, Y. J. Hu, and E. R. Bernstein, J. Chem. Phys. **124**, 024302 (2006).
[32] http//webbook.nist.gov/chemistry
[33] B. H. Torrie, S. X. Weng, and B. M. Powell, Mol. Phys. **67**, 575 (1989).
[34] T. Yamaguchi, K. Hidaka, and A. K. Soper, Mol. Phys. **97**, 603 (1999).
[35] S. Sarkar and R. N. Joarder, J. Chem. Phys. **99**, 2032 (1993).
[36] A. Arencibia, M. Taravillo, F. J. Perez, J. Nunez, and V. G. Baonza, Phys. Rev. Lett. **89**, 195504 (2002).
[37] Y. J. Shi, S. Consta, A. K. Das, B. Mallik, D. Lacey, and R. H. Lipson, J. Chem. Phys. **116**, 6990 (2002); F. Dong, S. Hienbuch, J. J. Rocca, and E. R. Bernstein, *ibid.* **124**, 224319 (2006).
[38] D. K. Havey and V. Vaida, J. Mol. Spectrosc. **228**, 152 (2004).
[39] Y. J. Shi, X. K. Hu, D. M. Mao, S. S. Dimov, and R. H. Lipson, Anal. Chem. **70**, 4534 (1998).
[40] S.-T. Tsai, J.-C. Jiang, M.-F. Lin, Y. T. Lee, and C.-K. Ni, J. Chem. Phys. **120**, 8979 (2004).
[41] N. Solca and O. Dopfer, J. Phys. Chem. A **109**, 6174 (2005).
[42] J.-W. Shin, N. I. Hammer, E. G. Diken, M. A. Johnson, R. S. Walters, T. D. Jaeger, M. A. Duncan, R. A. Christie, and K. D. Jordan, Science **304**, 1137 (2004).
[43] J. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson, and K. D. Jordan, Science **308**, 1765 (2005).